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Volatile Organic Hydrocarbon and Aldehyde Composition in Raleigh, North Carolina during the 1985 Woodsmoke Study

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16. ABSTRACT

Initial field tests for collection of volatile organic hydrocarbons and aldehydes under EPA's Integrated Air Cancer Project (IACP) were held in Raleigh, NC during the winter of 1985. Sampling was conducted during 12 hour (7:00-7:00) daytime or nighttime periods. Hydrocarbons were collected by pressurizing 6 liter "Summa polished" stainless steel cylinders. Aldehydes were collected as 2,4-dinitrophenylhydrazone (DNPH) derivatives using impingers and cartridge collection methods. Sampling locations included the primary outdoor site located in a residential neighborhood, a rural background site and inside and outside three homes operating wood stoves. Non-methane hydrocarbon levels at the primary site ranged from 150 to 850 ppbc while total carbonyls ranged from 3 to 35 ppb (v/v). Benzene levels ranged from 5 to 32 ppbc while formaldehyde levels ranged from 2-14 ppb. Hydrocarbon levels and distributions in the homes were similar inside and outside with a few noted exceptions. Carbonyl levels, however, generally were much higher inside than outside. The elevated carbonyl levels observed inside the homes is likely due to factors other than the presence of a wood stove.

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Introduction

The Integrated Air Cancer Project (IACP) is a long term interdisciplinary research program to develop scientific methods and databases for identifying the major sources of carcinogenic chemicals emitted into the air and/or arising from atmospheric transformation of chemicals emitted into the air.[1] Initial field studies[2] were conducted during the winter of 1985 in Raleigh, NC. Raleigh represented a simplified air shed impacted mainly by residential wood combustion and motor vehicle sources both of which can contribute substantially to the mutagenic activity found in ambient air samples. A limited amount of volatile organic hydrocarbon and aldehyde sampling was conducted during February and March 1985 while methods and protocols were being developed. Most samples were collected at the primary outdoor site located in a residential neighborhood and both inside and outside three homes operating wood stoves. A few samples were also collected at a rural background site. All sampling was conducted during 12 hour (7:00-7:00) daytime or nighttime periods.

Experimental Methods

Gas phase hydrocarbons were collected in 6 L "Summa" polished stainless steel canisters using a sampling apparatus similar to that described by Oliver.[3] The initially evacuated canisters were filled by pumping the sample through a flow controller at about 20 cc/min. resulting in a final pressure of about 21 psig after 12 hours. The canister samples were quantitatively analyzed by GC/FID using a modified Nutech model 320 cold-trap thermal-desorption system for sample concentration and injection. Typically, a 1.5- to 3.0-L sample was injected. The C2's and C3's were separated on a 12 foot by 1/8 inch stainless steel silica gel column maintained at 30°C while the rest of the hydrocarbons were separated on a Quadrex 100m by 0.5 mm soft glass capillary coated with 7.5% hydrophobic silica using a temperature program from -80 to +140°C.[4] Details of the hydrocarbon analytical procedures are available elsewhere.

Aldehydes were trapped as their 2,4-dinitrophenylhydrazine (DNPH) derivatives and analyzed by high performance liquid chromatography (HPLC). While a few aldehyde samples were initially collected using classical impinger techniques (acidified solution of DNPH in acetonitrile) for comparison, the majority of samples were collected using a cartridge technique. Briefly, prepacked silica gel cartridges were coated with an acidified solution of DNPH in acetonitrile (ACN) and excess solvent removed by blowing carbonyl-free nitrogen through the cartridges. The cartridges were used as direct probes and traps for sampling ambient air when the temperature was above 10°C, and a heated glass probe and manifold used when ambient temperatures were below 10°C. Sampling flow rates of 1L/min. were controlled using mass flow controllers or needle valves and a recording mass flow meter. The cartridges were eluted with 5 mL of ACN for analysis. Details on the cartridge sampling and analysis procedures have been reported.[5]

Results

The majority of sampling took place at night (7 P.M.-7 A.M.) at the Raleigh primary site. The primary sampling site (Quail Hollow Swim Club) was located in a residential neighborhood about one mile from two major roadways. Sampling periods encompassed a variety of meteorological conditions which affected the impact of wood stoves on air quality. Figure 1 shows the total NMHC levels in ppbc measured for several sampling

periods and hydrocarbon distribution by compound class. Both are plotted against the fine dichot particulate levels which varied from 19-129 $\mu g/m^3$. The fine particle loadings are an indication of wood smoke impact, with normal ambient levels in Raleigh being <25 ug/m3. (An atmospheric inversion leading to high wood smoke particulate levels does not of course necessarily mean that the vapor phase was also mostly wood smoke related. Mobile sources might also be expected to contribute substantially. The current data set, however, is too small to perform apportionment calculations on the vapor phase.) Total NMHC levels ranged from 150 to 840 ppbc but did not show any particular correlation with particulate levels although both did exhibit maxima for the same sample period. Paraffins are the most abundant class of hydrocarbons for all samples ranging between 49 to 60% of the total NMHC. Aromatic hydrocarbons were generally the second most abundant class ranging from 18 to 26% of total NMHC. Olefins ranged from 7 to 24% of total NMHC. Unidentified compounds typically averaged about 5% of the total NMHC. In general, the distribution observed for Raleigh is similar to those observed in 29 other urban areas across the country (sampling during summers of 1984 and 1985 between 6 A.M.-9 A.M.).[6] Benzene levels for these same sample periods ranged from 5 to 32 ppbc and averaged 3.1% of total NMHC.

Carbonyl concentrations observed at the primary site ranged from 3 to 35 ppb (v/v). Figure 2 shows the average distribution of carbonyls observed at the primary site. Formaldehyde, acetaldehyde, acetone, butyraldehyde, acrolein, propionaldehyde and x-butyraldehyde make up 95% of the total carbonyls. All the carbonyls in figure 2 which are preceded by an "x" indicate the summation of one or more unknown carbonyl derivatives which have retention times similar to known standards, e.g., one or more unknowns eluting near butyraldehyde between crotonaldehyde and benzaldehyde have been summed and labeled as x-butyraldehyde. Actual carbonyl levels observed on a ppb (v/v) basis were: formaldehyde 2 to 14; acetaldehyde 1 to 8; acetone 2 to 4; and acrolein 0.1 to 2.8. All other aldehydes generally were less than 1 ppb. Several aldehydes which we normally monitor were not detected at the primary site, i.e., hexanaldehyde, 2,5- dimethylbenzaldehyde and the three tolualdehydes.

Only a few hydrocarbon and aldehyde samples were concurrently obtained from the background site and primary site. The background site was located about 20 miles from the primary site in a rural area near Falls lake. All sampling periods at both sites corresponded to particulate levels <25 $\mu g/m3$. Class distribution of the NMHC's were about equal, but the total NMHC at the primary site averaged twice the background site. Total carbonyl levels were similar at the both sites for two of three sampling periods while the primary site level was twice the background site for the third sampling period. Background formaldehyde levels ranged from 0.9 to 1.4 ppb while the primary site values ranged from 1 to 2 ppb.

Three homes with wood stoves were selected for indoor microenvironment studies as part of the Raleigh effort. Concurrent samples were taken inside and outside each home to estimate exposures which may result from an inside source as opposed to intrusion of wood smoke from outside. All the homes in the study were occupied by non smokers. Residence #1 had a top loading free standing stove while residences #2 and #3 both had fireplace inserts. The air exchange rates for residences #1- #3, determined by SF_6, release were 0.42, 0.39, and 0.57 hr^{-1} respectively.

Table I lists some of the carbonyl and hydrocarbon data for the residence study. All samples were taken during the nighttime sampling period. Interferences were experienced with the chromatography of residence #3 hydrocarbon samples which prevented determining accurate distributions. The NMHC class distributions were similar for residences #1 and #2 except for the aromatics inside residence #1. This increase is

essentially due to a high concentration of naphthalene. Residence #1 had a noticeable smokey odor inside and the naphthalene levels may be related to wood stove emissions. Formaldehyde, acetone and acetaldehyde were the most prevalent carbonyls in all three homes except for residence #3 which had notably higher levels of two unknowns, x-valeraldehyde and x-dimethylbenzaldehyde. All three residences had much higher formaldehyde levels inside than out while both residence #1 and #3 generally had higher inside levels of all carbonyls relative to the concurrent samples from outside. Carbonyl samples obtained inside residences #2 and #3 during the daytime sample period (stoves not in active use) were similar to the nighttime sample period. This would seem to indicate inside carbonyl levels may not be effected by wood combustion as much as by other domestic activities such as cooking and/or particular furnishings or construction materials.

CONCLUSIONS:

The Raleigh IACP study relative to hydrocarbons and aldehydes resulted in some general observations with the caveat that the data set is limited.

1. The distribution of NMHC at the Raleigh primary site was similar to other U.S. cities.
2. Over 95% of the carbonyl levels measured were due to only 6 compounds of which formaldehyde, acetaldehyde and acetone were the most prevalent.
3. Carbonyl levels definitely appear higher inside homes and may not be related to wood combustion.
4. Elevated levels of naphthalene inside one home coincided with a noted smokey odor.

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TABLE I. HYDROCARBON AND CARBONYL DATA FROM RALEIGH RESIDENTIAL STUDY

	RESIDENCE #1		RESIDENCE #2		RESIDENCE #3	
	IN	OUT	IN	OUT	IN	OUT
% Paraffin	51.66	61.65	54.39	53.42	---	---
% Olefin	13.69	14.00	16.65	17.94	---	---
% Aromatic	26.81	14.05	19.84	21.36	---	---
Total NMHC (ppbc)	434.31	525.99	1081.14	911.28	---	---
Benzene (ppbc)	7.65	8.77	22.01	23.02	8.20	8.73
Naphthalene (ppbc)	30.05	1.57	3.03	2.88	0.36	1.54
Carbonyls (ppb, v/v)						
Formaldehyde	13.07	2.86	14.53	7.27	21.98	2.18
Acetaldehyde	5.16	1.34	4.80	4.44	8.46	1.25
Acrolein	1.94	0.31	0.63	1.47	0.74	0.18
Acetone	7.95	1.70	4.72	4.32	6.99	1.81
Propionaldehyde	0.67	0.22	0.54	0.67	0.91	0.21
Butyraldehyde	0.83	0.41	0.93	1.08	1.40	0.78
Benzaldehyde	0.13	0.05	0.11	0.27	0.41	0.12
x-Butyraldehyde	0.20	0.51	0.55	0.70	0.01	0.23
x-Valeraldehyde	0.37	0.26	0.33	0.40	3.97	0.19
x-Dimethylbenzaldehyde	1.07	0.20	0.97	0.65	4.30	0.43
Total Carbonyls	32.50	8.21	28.18	22.31	49.45	7.78

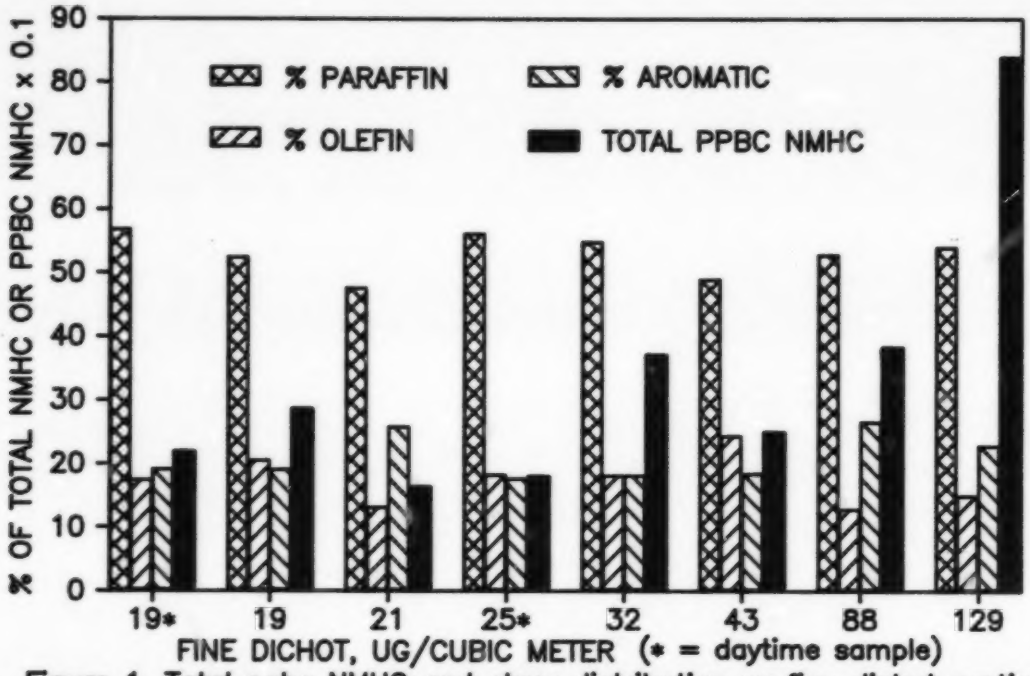

Figure 1. Total ppbc NMHC and class distribution vs fine dichot particulate concentrations observed at the Raleigh primary site.

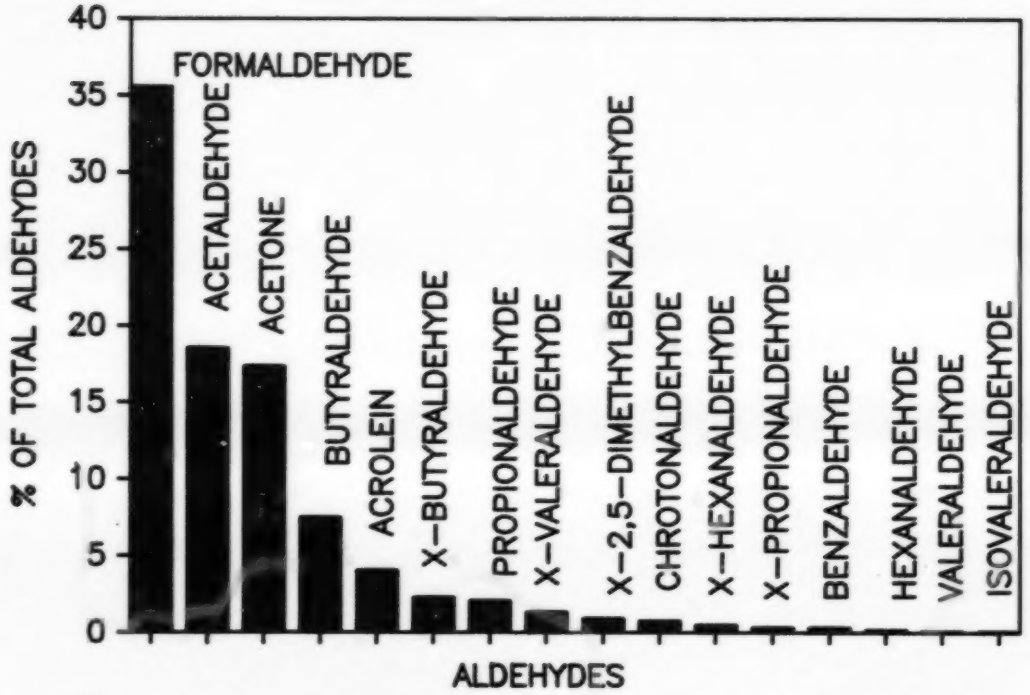

Figure 2. Average distribution of carbonyls at Raleigh primary site